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Simulated Precipitation Reference Materials II

J. K. Taylor, E. R. Deardorff, and T. C. Rains

National Bureau of Standards
Department of Commerce
Washington, D.C. 20234

September 1977

Final Report

Prepared for
The Environmental Protection Agency
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711

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This report describes the preparation of a series of reference materials for chemical analysis of natural precipitation. This is the second series of such materials prepared by NBS, under the sponsorship of EPA, and will be distributed by the latter as a means to intercalibrate atmospheric monitoring stations. The materials consist of ampoules of concentrates which can be diluted to simulate natural rainwater. A separate reference sample, to be used undiluted, is provided for evaluation acidity measurements. The analytical measurements made to establish the composition of the samples are also described.

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ABSTRACT

This report describes the preparation of a series of reference materials for chemical analysis of natural precipitation. This is the second series of such materials prepared by NBS, under the sponsorship of EPA, and will be distributed by the latter as a means to intercalibrate atmospheric monitoring stations. The materials consist of ampoules of concentrates which can be diluted to simulate natural rainwater. A separate reference sample, to be used undiluted, is provided for evaluation of acidity measurements. The analytical measurements made to establish the composition of the samples are also described.

1. INTRODUCTION

The analysis of the composition of rainfall and other forms of precipitation is an excellent means to monitor global atmospheric pollution. Such measurements must necessarily be made at widely spaced geographical locations, over extended periods of time, and by many independent investigators. It is imperative that the measuring stations be intercalibrated if the data obtained are to be correlated and combined for environmental interpretation. The measurement of a series of substantially identical samples by stations in a measurement system is an accepted method of evaluating laboratory performance for intercalibration purposes.

This report describes work done at the National Bureau of Standards under the sponsorship of EPA to prepare and establish the composition of a series of reference materials intended to be used for the intercalibration of precipitation measurement stations[1]. The materials consist of ampoules containing aqueous concentrates that simulate natural precipitation when accurately diluted. Three multicomponent solutions and one solution specifically designated for acidity measurement were prepared.

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[1] This work was performed at the National Bureau of Standards for the Environmental Protection Agency under Interagency Agreement EPA-IAG-D7-F1069.

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This is the second series of solutions prepared for the above described purpose. The details of the first series are contained in a report, NBSIR 75-958, "Simulated Precipitation Reference Materials", October 1975.

2. EXPERIMENTAL DETAILS

2.1 General Considerations

The reference materials are similar in concept to those prepared previously. While the former were satisfactory in most respects, laboratories had particular problems with the measurement of pH, conductivity and acidity. Accordingly, it was decided to prepare one reference material specifically intended for the measurement of these parameters. In addition, a series of three solutions was prepared containing a number of components at concentrations similar to those expected in natural samples.

The target compositions are given in Table 1. The solutions were prepared according to instructions furnished by EPA. Two of the solutions contain acids to stabilize them, while all three contain complexing agents to stabilize the iron, particularly. Although directions were followed implicitly, the third solution showed both immediate and long-term precipitation, so that the objectives were only partly realized.

2.2 Preparation of Reference Materials

The reference materials were prepared from high quality distilled water and reagent grade chemicals. The chemicals and quantities used are given in Table 2.

The instructions followed for preparation of Series 710000 and Series 720000 are as follows:

Dissolve all except the Pb salt in 1 liter of water. Mix well. Pipet 200 mL of this solution into each of two 2000 mL volumetric flasks, and dilute each solution to approximately 1800 mL. Dissolve the Pb salt in 100 mL water. Pipet 20 mL of the lead solution into each 2000 mL volumetric flask and dilute to volume. Mix well. Filter the two final solutions through Whatman 42 paper into four liter bottles.

Instructions for Series 730000:

Dissolve all except the Pb salt in approximately 3200 mL water. Dissolve the Pb salt in a separate portion of 200 mL water. Add the Pb solution to the first solution and dilute to four liters. Mix well. Filter the final solution through Whatman 42 paper into a four liter bottle.

The Series 730000 solution became cloudy when the sodium fluoride was added and a definite precipitate settled out. This was filtered off and analyzed spectrographically with the following result:

Ca >> 20%; Cu 1%; Fe 5%; Na 2%; Ni 1%, Si 1%; Zn 1%

The bulk solution was filtered before ampouling and appeared to be homogeneous at that time. However, a small amount of precipitate has settled out in the ampoules. Analysts are requested to shake the ampoules before opening and using. While there appears to be no difficulty with most of the constituents, the iron values appear to be questionable.

The Series 740000 bulk solution was prepared by dilution of the appropriate volume of 0.06N H_2SO_4 to a final volume of 20 liters. The sulfuric acid solution was standardized by titration with a 0.05 N NaOH solution that had been standardized with potassium acid phthalate, SRM 84. The acid was also standardized with respect to THAM, SRM 723.

The original intention was to deliver 20 mL of the bulk solution into ampoules. However, as explained in Section 2.3 it was necessary to dispense a smaller volume. The volume finally dispensed was 18.7 mL per ampoule so that each ampoule should contain 4.66 μeq of acid.

2.3 Ampouling

The bulk solutions were transferred to ampoules using an automatic dispensing and sealing machine of the Office of Standard Reference Materials. The ampoules used (Wheaton Cat. No. 176780) are made from borosilicate glass formulated to prevent a change of pH and to maintain the purity of the contents. They are pre-scored to eliminate the need for filing.

The dispensing equipment pumps the solution from the storage vessel and reproduceably injects a pre-set volume into the ampoules. Ampoules randomly selected for analysis were also weighed to verify the reproducibility of the filling operation. No significant changes were detected in the four solutions during the three hour filling operation. The dispensing equipment automatically flame-sealed the ampoules.

The ampoules used for Series 710000, Series 720000, and Series 730000 were of 10 mL capacity while 20 mL ampoules were used for the Series 740000 samples. The dispensing equipment was adjusted to deliver approximately 10 mL in the first group. It was intended to deliver 20 mL of the Series 740000 solution but a problem was encountered when the liquid splashed up into the necks of the ampoules during filling. This was eliminated when the volume was decreased to 18.7 mL.

The ampouling operation was very precise as indicated by the data of Table 3. The upward trend in mass delivered is due to the density differences in the respective solutions. The densities of the solutions were measured and the volumes calculated (which is the important parameter since the dispenser is a displacement device) are seen to be constant. The standard deviations for the first three series were pooled to calculate a two-sided tolerance interval of ± 0.2% at the 99% level. This means that there is a 99% confidence that 99% of the ampoules are within ± 0.2 percent of each other. The same tolerance level was found for the Series 740000 samples, which is to be expected, if the variation is based upon performance of the dispenser alone.

2.4 Numbering Sequence

The ampoules are labeled and numbered in the following sequences:

Series 710000 - 710001 to 710200
Series 720000 - 720001 to 720200
Series 730000 - 730001 to 730200
Series 740000 - 740001 to 740600

The rational of the numbering sequence is illustrated as follows:

710001

First digit: Fiscal year 1977
Second digit: Sample type 1,2,3, or 4
Remaining digits: Sample serial number, e.g., 0001

The samples were replaced in the individually compartmented boxes in which the ampoules were received from the manufacturer. Care was exercised to place them in the box in the order of filling. Samples for measurement were selected from these by a random number process. Altogether, 56 ampoules were selected from each Series 710000, Series 720000 and Series 730000 for this purpose, while 21 were

selected from the Series 740000. No differences were found in either mass content or composition that could be attributed to sequence of preparation. Accordingly, it is believed that the samples in each series are substantially uniform with respect to composition and total content.

The samples delivered to EPA were numbered sequentially, ignoring the gaps resulting from removal of the test samples. However, the actual production sequence could be ascertained should the need arise.

2.5 Analysis of Ampoules

Essentially seven ampoules were analyzed for each specific determination. However, for purposes of convenience, all measurements were not made on the same ampoule. The measurement data are summarized in Tables 4, 5, and 6. The methods used for measurement are summarized in the following subsections.

2.5.1 pH Measurements

The pH measurements were made on diluted samples of the concentrates for the 710000, 720000, and 730000 series; undiluted samples were used for the 740000 series. The combination pH electrode was calibrated with pH 4.01 and 7.00 buffers and the sample readings were taken directly from the digital pH meter display.

2.5.2 Conductivity Measurements

The conductivity measurements were made on samples similar to those used in the pH determinations. The cell constant, k, was determined using 0.01 M and 0.001 M KCl solutions having specific conductances, L, of 0.00141 and 0.000147 S cm^{-1}. The specific conductance of the sample solutions was calculated from the measured resistance at a frequency of 1 kHz by the equation:

$$L = \frac{k}{R} = \frac{0.307\ cm^{-1}}{R}$$

2.5.3 Acidity Measurements

Two ampoules of 740000 were broken open and emptied into a clean 100 mL beaker without washing the ampoules. This solution was titrated with standarized 0.01N NaOH to pH 8.3 using a research pH meter.

Each ampoule of 710000, 720000, and 730000 was diluted to 500 mL with distilled water and titrated with standarized 0.01N NaOH to pH 8.3 using a research pH meter. A blank correction was determined by titrating 500 mL of distilled water.

Typical titration curves are reproduced in figure 1. Curve 1 is for Series 710000, curve 2 is for Series 720000, and curve 3 is for Series 730000. The curve obtained when 30 μeq of acid is added to Series 730000 is also shown.

It is evident that the end point of pH 8.3 specified by water acidity methods does not correspond to the inflection point of the titration curve. The quantities of salts present exert a buffering effect and/or hydrolyze to distort the upper part of the titration curve. The values for acidity reported here are based on an arbitrary end point of pH 8.3, as specified by water analysis methods. However, the behavior shown in Figure 1 raises questions as to the meaning of such values.

When the Series 740000 ampoules were analyzed, the data appeared to fall into two groups. The acidity values for one of them was in close agreement with that for the bulk solution while the second group showed decreased acidity. In visual inspection some of the ampoules appeared to be slightly "brown" while the others appeared to be slightly "green". The ampoules with the "green" tinge showed the decreased acidity values.

The ampoules were supposedly from the same manufacturing lot and the producer has been unable to furnish an explanation for the color differences. While the difference in acidity was small, it could be predicted based on color selection of the ampoule. Accordingly, it was decided to remake the Series 740000 samples, using only one type of ampoule. The "brown" ampoules were used and the lot was screened before hand to exclude any of the "green" type.

The remarks above pertain only to the 20 mL ampoules used for containment of the Series 740000 samples. The 10 mL ampoules used for the other series appeared to be essentially colorless and no differential behavior was observed.

2.5.4 Analysis for Anions

2.5.4.1 Measurement of Sulfate Ion

Sulfate was determined by the Turbidimetric Barium Sulfate Method, developed by the Air and Industrial Hygiene Laboratory, State Department of Health, Berkeley, California. This method is similar to ASTM Method D 516-68 except a glycerol-alcohol-HCl solution is used to stabilize and promote precipitation of barium sulfate, instead of a glycerol and a sodium chloride solution.

2.5.4.2 Measurement of Nitrate Ion

Measurements for nitrate were made by the Brucine Method following the procedure in ASTM Method D 992-71, Nitrate Ion in Water. Nitrate ion reacts with brucine in strong sulfuric acid to develop a yellow color. A calibration curve was made with pure potassium nitrate to obtain a smooth curve in the range 0 to 250 µg/25 mL where the solution does not follow Beer's Law. The absorbance was read at 410 nm, using 1 cm cells. Undiluted samples were used in these measurements.

2.5.4.3 Measurement of Fluoride Ion

The fluoride determinations were performed by direct potentiometry on samples diluted 1:1 with TISAB (total ionic strength adjustment buffer). Calibration standards containing 2, 20, and 100 ppm F^- were also prepared by 1:1 dilution with TISAB to permit direct reading of the sample fluoride concentrations. The electrode response was Nernstian over this range and the emf readings on both samples and standards were generally stable.

2.5.4.4 Measurement of Chloride Ion

Chloride was determined by direct potentiometry using a chloride ion-selective electrode. Calibration standards containing 1, 10 and 100 ppm were used, and over the sample concentration range, the response was linear and approximately Nernstian.

2.5.5 Analysis for Cations

2.5.5.1 Measurement of Ammonium Ions

The technique used consisted of chemical measurement according to the procedure given in the following reference: C. O. Willits and C. L. Ogg, "1949 Report of Standarization of Microchemical Methods, Micro Kjeldahl Nitrogen Determinations", USDA Eastern Regional Research Laboratory, Philadelphia, PA. A micro-Kjeldahl steam distillation apparatus was used to separate the ammonia, released by sodium hydroxide, which was trapped in boric acid. The ammonia was titrated with standardized 0.01 N hydrochloric acid using methyl purple indicator.

2.5.5.2 Metals by Atomic Absorption and Flame Emission Spectrometry

All of the metallic cations were measured by atomic absorption or flame emission spectrometry. Measurements were made both on the bulk solution and on the ampoules. The contents of an ampoule were quantitatively transferred to a 100 mL volumetric flask. After addition of 1 mL of purified nitric acid, the solution was diluted to the calibrated volume. Emission or absorption measurements were made in duplicate. Calibration standards were made by dissolution of pure salts or pure metals.

3. ANALYTICAL RESULTS

The analytical results for Series 710000, Series 720000 and Series 730000 are summarized in Tables 4, 5, and 6. Each table contains the values calculated from the method of preparation where appropriate, and those obtained by measurement. The symbols used are as follows:

n = number of samples analyzed

$\bar{x}$ = average value by measurement

s = standard deviation of a single measurement

$\frac{ts}{\sqrt{n}}$ = 95% confidence interval of the average value

% = confidence interval expressed as percent of measured value

The values listed under $\bar{x}$ are the best estimates of various compositional parameters of the solution resulting from dilution of the concentrate of an ampoule to 500 ml.

The analytical values for Series 740000 samples are given in Table 7. The values reported are for samples as contained in the ampoules, without further dilution. The acidity values are based upon combining the contents of two ampoules. The pH and conductivity values are for undiluted samples but of course they are independent of the quantity of sample measured.

4. DISCUSSION

The samples in each series are believed to be substantially uniform in composition. Every ampoule in each series contains the same total amount of sample within narrow limits. Furthermore, the dilution of the contents, as indicated, should introduce no errors, provided high quality water is used for this purpose. Accordingly, the samples should be capable of evaluating between-laboratory variability within any requirement for precipitation analysis.

The various analysts at the National Bureau of Standards who examined the samples have had considerable experience with the methods used or ones very similar to them. Furthermore, the measurements were made as part of an ongoing program in trace analysis. Accordingly, the values indicated by x are believed to be unbiased and represent the best estimates of the compositional parameters.

When the measured values are compared with those based upon preparation of the solutions, the agreement is found to be good in most cases. The largest discrepancies are as follows:

Series	Constituent	Expected	Found
710000	K	.10	.199
710000	Na	.10	.151
720000	Na	2.0	2.86
730000	Fe	.18	.076

Because of the visible brown precipitate in the Series 730000 ampoules, the value obtained for Fe is probably meaningless. The data for the other discrepant values were reexamined but no fault could be found in them. Accordingly, the measured values are believed to be valid.

The negligible variation in the total contents of the ampoules, and the fact that they are filled with true solutions (except as already noted for Series 740000), leads to the conclusion that there are no systematic differences between ampoules in each series. Random errors can arise from possible instability of the solution during long-term storage, although advance precautions have been taken to minimize this source of error. A number of ampoules have been reserved at the National Bureau of Standards for future study, should this appear to be desirable.

5. RE-EXAMINATION OF FY 76 SAMPLES

During the course of analysis of the present samples, a limited number of measurements were made on ampoules remaining from the lot prepared in October 1975. The results are given in Table 8 under the columns identified as 7/77. The values reported in October 1975, in the columns identified 10/75, are given for comparison.

The results for SO_4 and NO_3 were measured on the ion chromatograph and kindly furnished to us by Mr. James Mulick, EPA, Research Triangle Park, NC, while the remainder were obtained at NBS. The only constituents that have shown large decreases are lead and copper. This is constistent with the results reported earlier and predicted at the time of preparation of the samples. There has been an apparent small decrease in the calcium concentrations but the sodium concentrations have shown only a small increase. These solutions had all shown a slight initial increase in sodium, presumably from interaction with the ampoules, but this change has apparently not continued.

The overall conclusion that may be drawn is that concentrates of this kind show sufficient stability, with several exceptions, for use as intercalibration samples. These samples contained no stabilizers. The present samples, containing acid as a stabilizer, are expected to be more stable than the previous ones.

6. INSTRUCTIONS FOR USE

6.1 Series 710000, Series 720000, Series 730000

The samples consist of ampoules of concentrates which simulate rainwater, when diluted to 500 mL. The ampoules are pre-scored at the constriction to facilitate breaking off the tip. Glassware should be thoroughly cleaned and rinsed with distilled water before use. The distilled water used for rinsing and dilution should be of the highest quality since any impurity will add to the constituents of the sample. The recommended procedure for preparation of the test sample is as follows:

1. Rinse the outside of the ampoule to remove dust and allow to air dry.

2. Hold ampoule in a vertical position, tip over and back, and gently tap to transfer any liquid from the tip to the body of the ampoule.

3. Hold ampoule with a paper towel (a precaution to prevent injury tc hand) and snap off the tip at the scored constriction.

4. Place a clean funnel in the neck of a clean 500 ml volumetric flask and transfer the contents of the ampoule, with gentle shaking as required to facilitate removal of liquid.

5. Rinse the ampoule two times with distilled water and transfer the rinsings to the flask.

6. Add distilled water to the flask to dilute to the graduation mark, and mix contents thoroughly.

7. Treat the resulting solution with the same care and in the same manner as a sample of natural rainwater.

6.2 Series 740000

The solutions are intended for use without additional dilution.

6.2.1 Acidity Measurement

Empty the contents of two ampoules into a clean 100 mL beaker, according to instructions 1, 2, and 3 in Section 6.1. Hold the inverted ampoule over the beaker until contents have drained as much as possible. Check for visible inclusions of solution in the ampoule and shake again, if required. Any film of solution remaining in the ampoule will not cause significant error.

6.2.2 Conductivity and pH Measurements

Empty the contents of one ampoule into a clean 30 mL beaker. Remove substantially all the contents by shaking as directed before. However, the measurements are not influenced by the quantity of sample used, hence quantitative delivery is not required. It is convenient to measure sample conductivity, followed by measurement of pH on the same sample.

7. ACKNOWLEDGEMENTS

The participation of the following members of the Staff of the Analyical Chemistry Division in analysis of these reference materials is gratefully acknowledged: R. A. Durst; J. D. Messman; T. J. Brady. Mr. W. P. Reed of the NBS Office of Standard Reference Materials was responsible for ampouling the samples.

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Table 1. Target Compositions

Unit of Concentration: mg/L

Constituent	Series 710000	Series 720000	Series 730000
pH	---	---	---
Conductivity	---	---	---
Acidity	---	---	---
SO_4 (S)	2.9 (.96)	8.8 (2.9)	9.8 (3.23)
NO_3 (N)	.37 (.083)	3.2 (.71)	15.0 (3.4)
NH_4 (N)	.11 (.085)	1.07 (.83)	10.4 (8.1)
Cl	1.0	6.4	40.0
F	.048	.095	.30
Ca	.10	1.0	8.0
Cd	.022	.056	.10
Cu	.032	.19	.98
Fe	.022	.068	.18
K	.10	.98	5.0
Mg	.10	1.0	---
Mn	.027	.055	.083
Na	.10	2.0	10.0
Ni	.029	.088	.50
Pb	.021	.10	1.0
Zn	.033	.20	1.0

Table 2. Preparation of Stock Solutions

Chemical	710000 Grams	720000 Grams	730000 Grams
$CaCl_2 \cdot 2H_2O$	0.1838	1.8375	5.8652
NaCl	0.0585	3.060	1.9892
NaF	0.0525	0.105	.1344
$MgSO_4 \cdot 7H_2O$	0.5043	5.043	--
KNO_3	0.2525	1.2625	2.5664
NH_4Cl	0.154	1.540	6.1160
$Zn(NO_3)_2 \cdot 6H_2O$	0.0744	0.4463	.9224
$Cd(NO_3)_2 \cdot 4H_2O$	0.0309	0.0771	.0616
$Cu(NO_3)_2 \cdot 3H_2O$	0.0604	0.3624	.7488
Ferric Ammonium Citrate	0.0648	0.1945	.2076
$MnCl_2 \cdot 4H_2O$	0.495	0.099	.0496
$Ni(NO_3)_2 \cdot 6H_2O$	0.0728	0.2183	.4948
$PbAc_2 \cdot 3H_2O$	0.0190	0.0948	.3792
$NaNO_3$		0.425	.5952
Na_2SO_4			.2982

710000 H_2SO_4	26,900 micro-equivalents added from a standard solution.
HCl	7,300 micro-equivalents added from a standard solution.
720000 H_2SO_4	51,000 micro-equivalents added from a standard solution.

Table 3. Precision of Ampouling

Series	n	$\bar{x}$, g	s, g	Volume, mL	Pooled s	$\frac{ts}{\sqrt{n}}$	%
710000	7	9.975	.0027	10.01			
720000	7	9.980	.0042	10.01	.0039	.024	0.24
730000	7	10.003	.0045	10.02			
740000	7	18.7012	.0081	18.7		.039	.21

Table 4. Analytical Data for Series 710000

Constituent	Unit	By Preparation	By Measurement n	$\bar{x}$	s	$\frac{ts}{\sqrt{n}}$	%
pH			5	4.48	.13	.17	3.7
Conductivity	$\mu S \cdot cm^{-1}$		5	28.84	.48	.62	2.1
Acidity	μeq/ampoule		7	37.57	1.10	1.06	2.8
SO_4	mg/L	2.9	5	2.66	.17	.22	8.2
SO_4(S)	mg/L	.96	5	.89	.05	.06	8.2
NO_3	mg/L	.37	3	.503	.005	.011	2.2
NO_3(N)	mg/L	.083	3	.114	.001	.0023	2.2
NH_4	mg/L	.11	7	.107	.0028	.0027	2.5
NH_4(N)	mg/L	.085	7	.084	.0021	.0020	2.5
Cl	mg/L	1.0	8	1.35	.092	.080	5.9
F	mg/L	.048	7	.0461	.00069	.00067	1.4
Ca	mg/L	.078	7	.0766	.00090	.00086	1.1
Cd	mg/L	.022	7	.0230	.00010	.00010	.4
Cu	mg/L	.032	7	.0360	.00046	.00044	1.2
Fe	mg/L	.022	7	.0214	.00018	.00018	.8
K	mg/L	.10	7	.199	.00111	.0010	.5
Mg	mg/L	.10	7	.110	.00034	.00032	.3
Mn	mg/L	.027	7	.0296	.00024	.00022	.7
Na	mg/L	.10	7	.151	.0060	.0058	3.8
Ni	mg/L	.029	7	.0338	.00056	.00054	1.6
Pb	mg/L	.021	7	.0232	.00062	.00060	2.5
Zn	mg/L	.033	7	.0344	.00024	.00022	.6

Table 5. Analytical Data for Series 720000

Constituent	Unit	By Preparation	By Measurement n	$\bar{x}$	s	$\frac{ts}{\sqrt{n}}$	%
pH			7	4.08	.029	.028	0.7
Conductivity	$\mu S \cdot cm^{-1}$		7	77.9	.65	.63	.8
Acidity	ueq/ampoule		7	59.94	.35	.34	.6
SO_4	mg/L	8.8	6	7.90	.58	.64	8.0
SO_4(S)	mg/L	2.9	6	2.64	.20	.21	8.3
NO_3	mg/L	3.2	6	3.02	.0	0	-
NO_3(N)	mg/L	.71	6	.68	.0	0	-
NH_4	mg/L	1.07	7	1.07	.0049	.0047	.4
NH_4(N)	mg/L	.83	7	.82	.0049	.0047	.5
Cl	mg/L	6.4	8	7.22	.22	.19	2.6
F	mg/L	.095	7	.0997	.0026	.0025	2.5
Ca	mg/L	.78	7	.766	.0072	.0070	.9
Cd	mg/L	.056	7	.0572	.00046	.00044	.8
Cu	mg/L	.19	7	.192	.0013	.00012	.6
Fe	mg/L	.068	7	.0612	.00058	.00056	.9
K	mg/L	.98	7	.994	.0084	.0082	.8
Mg	mg/L	1.0	7	1.12	.0040	.0038	.3
Mn	mg/L	.055	7	.0586	.00026	.00026	.4
Na	mg/L	2.0	7	.286	.014	.014	.5
Ni	mg/L	.088	7	.0948	.0011	.0011	1.1
Pb	mg/L	.10	7	.0988	.00028	.00028	2.8
Zn	mg/L	.20	7	.198	.00028	.00028	1.4

Table 6. Analytical Data for Series 730000

Constituent	Unit	By Preparation	By Measurement n	$\bar{x}$	s	$\frac{ts}{\sqrt{n}}$	%
pH			7	5.98	.026	.025	4.2
Conductivity	$\mu S\ cm^{-1}$		7	190.5	8.8	8.5	4.5
Acidity	μeq/ampoule		7	52.5	1.8	1.7	3.3
SO_4	mg/L	9.8	4	9.94	.44	.70	7.1
SO_4(S)	mg/L	3.23	4	3.32	.14	.22	6.8
NO_3	mg/L	15.0	4	14.50	.082	.131	.9
NO_3(N)	mg/L	3.4	4	3.27	.021	.034	1.0
NH_4	mg/L	10.4	7	10.18	.034	.032	3.1
NH_4(N)	mg/L	8.1	7	7.93	.028	.027	3.4
Cl	mg/L	40	7	42.4	3.3	3.2	7.5
F	mg/L	.30	7	.103	.0032	.0031	3.0
Ca	mg/L	6.24	7	5.98	.048	.046	.8
Cd	mg/L	.10	7	.114	.00048	.00046	.4
Cu	mg/L	.98	7	1.012	.0102	.0098	1.0
Fe	mg/L	.18	7	.076	.017	.016	20
K	mg/L	5.0	7	4.94	.056	.054	1.1
Mg	mg/L	---					
Mn	mg/L	.083	7	.0846	.0003	.00028	.3
Na	mg/L	10.0	7	9.66	.042	.040	.4
Ni	mg/L	.50	7	.518	.0072	.0070	1.3
Pb	mg/L	1.0	7	1.04	.0088	.0084	8
Zn	mg/L	1.0	7	1.05	.0096	.0092	.9

Table 7. Compositional Data for Series 740000

Constituent	Unit	n	$\bar{x}$	s	$\frac{ts}{\sqrt{n}}$	$\frac{s}{\bar{x}}$
pH		7	3.81	.037	.036	0.9
Conductivity	$\mu S\ cm^{-1}$	7	8.00	5.9	5.7	7.1
Acidity	μeq/ampoules two	7	9.32	.18	.17	1.8

Table 8. Re-examination of FY76 Samples

Constitutent	A		B		C		D	
	10/75	7/77	10/75	7/77	10/75	7/77	10/75	7/77
SO_4(S) µg/L	342	365	1188	1267	1672	1667	3333	3300
NO_3(N) µg/L	26	33	150	158	1499	1501	2457	2461
Na µg/L	153	166	516	546	2460	2540	5444	5460
K µg/L	63	66	102	107	1007	1010	3058	2920
Ca µg/L	99	84	442	370	1230	1040	2840	2420
Mg µg/L	86	86	456	454	729	712	922	936
Zn µg/L	21	20	95	89	307	284	610	626
Cd µg/L	30	30	116	115	578	576	1010	990
Cu µg/L	52	40	88	35	200	104	393	174
Ni µg/L	21	22	104	113	506	560	1007	1034
Pb µg/L	18	8.8	88	58	152	105	110	62
Mn µg/L	52	54	81	85	100	103	200	204

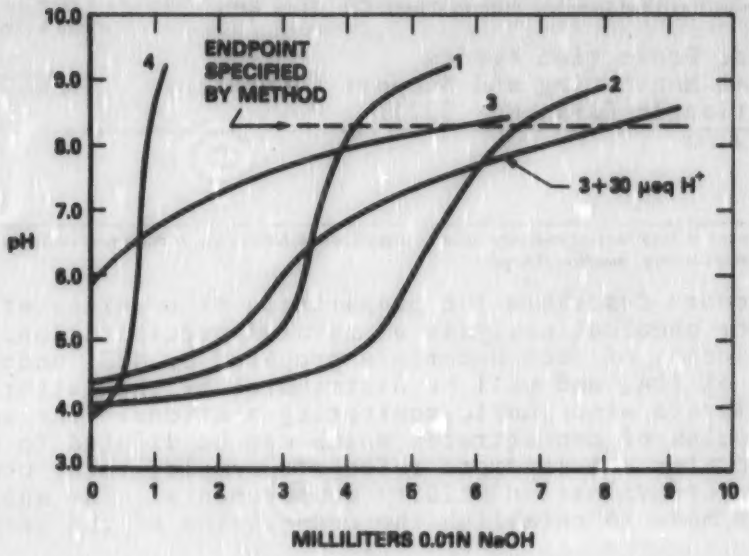

Figure 1. Titration curves for acidity measurements